PLATINUM AND INORGANIC PLATINUM COMPOUNDS

Analyte:	Platinum and inorganic platinum compounds	Method No.:	
		Range:	0.00079-0.0031 mg/m^3
Matrix:	Air	Precision:	
OSHA Standard:	0.002 mg/m^3	Validation Date:	8/29/75
Procedure:	Filter collection, acid digestion, AA/high temperature graphite atomization	Revised:	3/25/81

1. Synopsis

1.1 A known volume of air is drawn through a cellulose membrane filter to collect the analyte.

1.2 The sample-containing filters are wet-ashed using nitric acid to dissolve the organic matrix; platinum and its compounds are then solubilized in either nitric-perchloric or nitric-hydrochloric acid solutions; platinum dioxide-containing samples are subjected to pre-ashing at 550 °C.

1.3 The solutions of samples and standards are analyzed by flameless atomic absorption spectroscopy using a heated graphite atomizer. A hollow cathode lamp is used to provide a characteristic platinum line at 265.9 nm.

1.4 The samples must be carefully interspersed with calibration standards which give about the same response as the samples in order to obtain reliable results.

2. Working Range, Sensivity, and Detection Limit

2.1 The working range for standard platinum solution using atomic absorption spectrometry as described (electrothermal atomization) is 0.01-0.20 µg/mL. The method was validated with potassium hexachloroplatinate (K_2PtCl_6) over the range of 0.00079-0.0031 mg/m^3 at an atmospheric temperature and pressure of 24 °C and 767 mm Hg using a 720-L sample. Under the conditions of sample size (720 L), the linear working range of the method is estimated to be 0.0004-0.0060 mg/m^3 when the total sample collected is diluted to 25-mL and a 50-µL aliquot is analyzed.

The detection limit of the method using a 25-mL final solution volume is 0.10 µg platinum/sample, which corresponds to 0.00014 mg/m^3 assuming a 720-L sample. The sensitivity is 0.003 µg/mL for 1% absorption. The method may be extended to higher values by dilution of the sample. Measurement of lower atmospheric concentrations can be made by using smaller final solution volumes, by longer sampling times, or by scale expansion to increase instrumental response.

3. Interferences

There are no known interferences to the platinum assay using the high-temperature graphite accessory.

4. Precision and Accuracy

Using potassium hexachloroplatinate, the coefficient of variation ($\overline{CV}_T$) for this method in the range of 0.00079-0.0031 mg/m^3 was 0.062. This value corresponds to a 0.00012 mg/m^3 standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in References 11.1 and 11.2.

A collection efficiency of 99.7 ± 0.6% was determined for the collection medium; thus, no bias was introduced in the sample collection step. Analytical recoveries less than 95% (Section 4.3) are to be accounted for by using the appropriate recovery factors (Sections 8.4 and 10.3). With these corrections made, ($\overline{CV}_T$) is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

Analytical recoveries for the platinum species evaluated are as follows: platinum metal, 94% (8.3.2b); ammonium tetrachloroplatinate, 94% (8.3.2a); platinum dioxide, 98% (8.3.2c); potassium hexachloroplatinate, 97% (8.3.2a).

5. Advantages and Disadvantages

The method is tedious and requires a high degree of technical skill; however, it is the only one sensitive enough to analyze personal air samples.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the collection of personal air samples for the determination of metal content has the following components:

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and 37-mm, three-piece cassette filter holder.

Personal sampling pump. A calibrated personal sampling pump whose flow can be determined to an accuracy of ± 5% at the recommended flow rate. The pump must be calibrated with a filter holder and filter in the line.

Thermometer

Manometer.

6.1.5 Stopwatch.

6.2 Mixed cellulose ester membrane filter, 37-mm diameter, 0.8 µm pore size.

6.3 Atomic absorption spectrophotometer having a direct readout (or recorder output) proportional to absorbance units, graphite furnace accessory and deuterium background corrector accessory. The use of a background corrector is absolutely necessary in order to avoid false positive signals from molecular scatterings at the 265.9 nm wavelength.

6.4 The platinum radiation source used is a hollow cathode lamp; the line chosen for analysis is 265.9 nm.

6.5 An electronic integrator, or some other suitable method for measuring peak areas.

6.6 Automatic or manual micropipettor for accurately injecting 50-µL sample aliquots into the graphite furnace tube.

6.7 Glassware, borosilicate.

6.7.1 125-mL Phillips beakers with watchglass covers.

6.7.2 Pipets, delivery or graduated: 1-, 5-, 10-mL.

6.7.3 25-mL volumetric flasks.

6.7.4 50-mL quartz crucibles with covers.

6.8 Adjustable, thermostatically-controlled hot plate capable of reaching 400 °C.

6.9 Oven or muffle furnace capable of reaching 550 °C.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

Dist· led or deionized water.

Concentrated nitric acid.

Perchloric acid

Hydrochloric acid.

Nitric acid: perchloric acid mixture (2 parts HNO_3 + 1 part $HClO_4$).

Nitric acid: hydrochloric acid mixture (1 part HNO_3 + 1 part HCl).

Platinum standards.

7.7.1 Platinum standard stock solution, 1000 µg/mL, commercially available.

7.7.2 Dilute platinum stock solution, 1 µg/mL. Prepare by appropriate (preferably sequential) dilution of above solution. Prepare fresh daily in 0.01 M nitric acid.

7.7.3 Prepare a series of working standards by adding 0.5-3.0 µg of platinum to 25-mL volumetric flasks. Depending on the dissolution procedure used, either add: a) 0.5 mL concentrated nitric-perchloric acid and dilute to volume with distilled water (refer to Section 8.3.2a); or b) 2 mL nitric-hydrochloric acid mixture and dilute to volume with distilled water (refer to Section 8.3.2b). These standards should be prepared fresh daily.

8. Procedure

8.1 Cleaning of Equipment

8.1.1 Before use, all glassware should initially be soaked in a mild detergent solution to remove any residual grease or chemicals.

8.1.2 After initial cleaning, the glassware should be thoroughly rinsed with warm tap water, aqua regia, tap water, and distilled water, in that order, and then dried.

For glassware which has been subjected to the entire cleaning procedure, aqua regia and water rinses will be adequate.

8.2 Collection and Shipping of Samples

8.2.1 Each personal sampling pump must be calibrated with a representative filter cassette in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.2.2 Assemble the filter in the three-piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad.

8.2.3 Remove the cassette plugs and attach to the personal sampling pump tubing. Clip the cassette to the worker's lapel. The cassette plugs are replaced after sampling.

8.2.4 Air being sampled should not pass through any hose or tubing before entering the filter cassette.

A sample size of 720 L is recommended. Sample at a flow rate of 1.5-2.0 Lpm. The flow rate should be known with an accuracy of ± 5%.

Turn the pump on and begin sample collection. Since it is possible for a filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and the sampling should be terminated at any evidence of a problem.

8.2.7 Terminate sampling at the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation.

8.2.8 Carefully record the sample identity and all relevant sampling data.

8.2.9 With each batch of ten samples, submit one filter from the same lot of filters which was used for sample collection and which is subjected to exactly the same handling as the samples except that no air is drawn through it. Label this as a blank.

8.2.10 The cassettes in which the samples are collected should be shipped in a suitable container designed to prevent damage in transit.

8.3 Analysis of Samples

8.3.1 Open the cassette filter holder and carefully remove the cellulose membrane filter from the holder and cellulose backup pad with the aid of tweezers and transfer the filter to a 125-mL Phillips beaker.

8.3.2 Wet ashing and digestion. If the sample is expected to contain platinum dioxide, proceed to (c) below; otherwise, destroy the organic filter matrix by treating the sample in each beaker with 2 mL of concentrated HNO_3. Cover each beaker with a watchglass and heat on a hot plate (140 °C) in a fume hood until all the filter is dissolved and the volume is reduced to about 0.5 mL. Repeat this process once more using 2 mL of HNO_3. Cool the beaker and contents.

a. If the platinum salts expected to be present are known to be readily soluble, for example, platinates, add 3 mL of HNO_3-$HClO_4$ mixture and continue evaporating to fumes to effectively complete digestion of the filter. Do not allow the solution to evaporate to dryness at any point. Platinum metal will not, however, be recovered (recovery < 5%) by this step.

b. For platinum metal or those platinum salts that are not solubilized employing the nitric acid-perchloric acid procedure, the following procedure should be employed. That is, after destruction of the organic filter matrix, add 2 mL of an equal volume mixture of concentrated nitric and hydrochloric acids and warm slightly for one minute. Then proceed to 8.3.3.

c. Place the filter in a 20-mL quartz crucible. Destroy the filter matrix with nitric acid as described above. Place a cover on each crucible and transfer the crucibles to a muffle furnace or oven capable of attaining 550 °C. Raise the temperature to 550 °C and maintain for eight hours or overnight. Allow each crucible to cool to room temperature. Dissolve the residue as described in (b) above.

8.3.3 Cool solutions and add 10 mL of distilled or deionized water to each one.

Quantitatively transfer the clear solutions into 25-mL volumetric flasks.

8.3.5 Rinse each beaker or crucible at least twice with 5-mL portions of distilled water, and quantitatively transfer each rinsing to the solution in the volumetric flask and dilute to 25 mL.

Spectrophotometric measurements.

a. The instrumental parameters for source power, background corrector, and furnace alignment, as well as furnace parameters such as inert gas flow and time/temperature conditions for drying and atomization, should be established in accordance with the manufacturer's recommendations. Note, however, that in order to avoid premature loss of platinum the following drying and charring conditions should be observed:

Sample Cycle	Time in Seconds	Temperature (°C)
Sample drying	40	150
Sample charring	20	500
Sample atomization	10	2700

b. Inject a 50-µL aliquot of the sample solution into the graphite tube using a micropipet.

c. A minimum of two injections/sample should be done.

d. To obtain reliable results, samples must be frequently alternated with standards which give responses close to that of the sample. The experimental protocol recommended is as follows: inject a standard solution in duplicate, inject a sample in duplicate, reinject standard in duplicate, etc.

NOTE: The characteristics of the graphite tubes can influence the results drastically. Careful attention must be paid to the response of the standard (i.e., if the graphite tube gives erratic results and non-reproducible peak areas, it must be rejected and replaced because results so obtained are not reliable).

8.3.7 Measurement of area. The area of the absorption peak is measured by some suitable form of area measurement, such as a planimeter or an electronic integrator. Note that the peak height measurements will give somewhat poorer precision as peak shapes change with the aging of the graphite tube.

8.3.8 Appropriate filter blanks must be analyzed by the same procedure used for the samples.

Determination of Sample Recovery

8.4.1 Need for determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of the analyte. The analyte recovery should be determined in duplicate and should cover the concentration ranges of interest. If the recovery of the analyte is less than 95%, the appropriate correction factor should be used to calculate the true value.

8.4.2 Procedure for determining recovery. A known amount of the analyte, preferably equivalent to the concentration expected in the sample, is added to a representative cellulose membrane filter and air-dried. The analyte is then recovered from the filter and analyzed as described in Section 8.3. Duplicate determinations should agree within ± 5%.

In the original validation study, an amount of K_2PtCl_6 equivalent to that present in a 720-L sample at the selected level was used for the recovery studies. Six filters at each of the three levels (0.5X, 1X, and 2X the OSHA standard) were spiked accordingly. All filters were then digested and analyzed as described in Section 8.3.2a with a mean recovery of 97.2%.

The recovery equals the weight in µg recovered from the filter divided by the weight in µg added to the filter, or:

$$\text{Recovery} = \frac{\text{Average weight (µg) recovered}}{\text{Weight (µg) added}}$$

9. Calibration and Standardization

Prepare a series of working standards containing 0.5-3.0 µg of platinum in 25 mL of dilute acid mixture. Refer to Section 7.7.3.

The appropriate calibration standards are alternately analyzed with the samples to determine the response factor. This practice will minimize the effect of observed fluctuations or variations in absorbance and peak width readings during any given day.

10. Calculations

Determine the weight in µg corresponding the absorbance area of the sample by using the appropriate response factor for the sample.

10.2 Corrections for the blank must be made for each sample

$$\mu g = \mu g \text{ sample} - \mu g \text{ blank}$$

where: µg sample = µg found in sample filter.
µg blank = µg found in blank filter.

10.3 Divide the total weight by the recovery to obtain the corrected µg/sample.

$$\text{Corrected } \mu g/\text{sample} = \frac{\text{Total weight}}{\text{Recovery}}$$

10.4 Determine the volume of air sampled at ambient conditions in liters based on the appropriate information such as flow rate in Lpm multipled by sampling time. If a pump using a rotameter for flow rate control was used for sample collection, a pressure and temperature correction must be made for the indicated flow rate. The expression for this correction is:

$$\text{Corrected Volume} = f \times t \left(\frac{P_1}{P_2} \times \frac{T_2}{T_1} \right)^{1/2}$$

where: f = flow rate sampled.
t = sampling time.
P_1 = pressure during calibration of sampling pump (mm Hg).
P_2 = pressure of air sampled (mm Hg).
T_1 = temperature during calibration of sampling pump (°K).
T_2 = temperature of air sampled (°K).

10.5 The concentration of the analyte in the air sampled can be expressed in mg/m^3 ($\mu g/L = mg/m^3$).

$$mg/m^3 = \frac{\text{Corrected } \mu g \text{ (Section 10.3)}}{\text{Air volume sampled (L)}}$$

11. References

11.1 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.2 Heavy Metal Aerosols: Collection and Dissolution Efficiencies, NIOSH Contract 210-79-0058, W. F. Gutknect, M. H. Ranade, P. M. Grohse, A. Damle, D. O'Neal, Research Triangle Institute, Research Triangle Park, North Carolina 27709, March, 1981.